# HIGH STRENGTH TITANIUM COPPER ALLOY, MANUFACTURING METHOD THEREFOR, AND TERMINAL CONNECTOR USING THE SAME

#### BACKGROUND OF THE INVENTION

Field of the Invention

[0001] The present invention relates to high strength titanium copper alloys, which are superior in bending properties, used for terminal connectors and other electronic components, a manufacturing method therefor, and a terminal connector using the same. The invention also relates to high strength titanium copper alloys, which are optimal for a fork-shaped contact demanding high strength for raw material of metal material, a manufacturing method therefor, and a fork-shaped connector using the titanium copper alloy.

## Description of the Related Art

[0002] Copper alloy containing titanium such as C1990 (hereinafter called titanium copper alloy) is noted for its superior workability and mechanical strength, and is widely used in terminal connectors and in other applications for electronic components. On the other hand, the trend toward miniaturization of electronic components is recently stronger than before, and the wrought product of copper alloys for electronic components are required to be even thinner in thickness to cope with this trend. In a view of the thinness of material, higher strength of the material itself is required to maintain the contact pressure of the connector, and a small bending radius is required in the bending process of components to fulfil

the function in a limited space. That is, the titanium copper alloy is required to have contrary characteristics of high electrical conductivity and high strength and superior bending properties.

[0003] Furthermore, along with the advancement in high density mountings for cellular phones, digital cameras, video cameras, etc., metal members for electronic components such as terminal connectors and lead frames are bent and formed in very complicated shapes, and an superior bending properties is required, in particular, in addition to having high strength.

[0004] Under such circumstances, in order to improve bending properties and the stress relief rate of the titanium copper alloy, much has been reported about the manufacturing method of solution treatment of crystals, under heat treatment condition, not exceeding a grain size of 20  $\mu$ m (for example, Japanese Patent Application Laid-Open No. 7-258803). However, to satisfy the requirement of bending properties of the copper alloy material used in recent electronic components such as terminal connectors, at present, such an improved titanium copper alloy does not have sufficient bending properties. To satisfy the requirements for titanium copper alloy, it is important to improve the correlation of strength and bending properties, and for this purpose, it is also necessary to improve the manufacturing method for titanium copper alloy.

[0005] Hitherto, where the required tensile strength of copper alloy for electronic component was at a medium level of about 500 to 800 MPa, brass, phosphor bronze, or nickel silver is used, or where a higher electrical conductivity is required, Cu-Ni-Si, Cu-Cr-Zr, or Cu-Cr-Sn copper alloy is used, and where a high strength over about 900 MPa is required, beryllium copper or titanium copper is used.

[0006] Recently, demand for FPCs (flexible printed circuit boards) is increasing, and the connectors for FPCs are modified. The fork-shaped connector is used in a connector for an FPC, and in contrast to the general-purpose connector used on the surface contacting with metal material, it is designed to contact with the circuit board on the fracture of the copper alloy plate. Accordingly, a bending process is not necessary, and the fork-shaped connector is required to have a high strength, in the first place, if the bending properties are not favorable.

[0007] Specifically, the fork-shaped connector is required to have a tensile strength of at least 1000 MPa or more, and in order to be applicable to versatile designs, a tensile strength of 1200 MPa or more is necessary.

[0008] Stainless steel of high strength, for example, SUS301 has a tensile strength exceeding 1200 MPa, but stainless steel is low in electrical conductivity, about 2.4% IACS, and cannot be used for a fork-shaped connector. A fork-shaped connector is required to have an electrical conductivity of at least 10% IACS.

[0009] As a copper alloy having a tensile strength of 1200 MPa or more, beryllium copper is well known. As a high strength copper alloy, titanium copper is also usable, but in order to have a tensile strength of 1200 MPa or more, titanium must be contained at 4% by mass, and it further requires special treatment such as MTH (aging, working, heating) (Lecture on Modern Metal Materials 5, Nonferrous Materials, p. 78 (Japan Society of Metallurgy), etc.).

[0010] However, titanium copper containing Ti at 4% by mass is poor in workability, and is likely to crack in hot rolling or to develop edge cracks in cold rolling, and it is difficult to manufacture at high proof stress industrially, and it is also difficult to sell commercially as material for

electronic components. The MTH treatment is a process of cold rolling of titanium copper after aging, followed by heat treatment, but cold rolling of titanium copper alloy after aging is likely to cause edge cracking, and it is difficult to manufacture.

[0011] On the other hand, in the conventional manufacturing method for titanium copper containing 3% by mass of Ti (C1990), the obtained tensile strength is about 1000 MPa at most. Japanese Patent Application Laid-Open No. 7-258803 discloses a manufacturing method of solution treatment of titanium copper alloy in the heat treating condition in which the crystal grain does not exceed  $20\,\mu\text{m}$ , and it is known that a material which is superior in bending properties and is not lowered in strength can be manufactured as compared with similar conventional materials; however, titanium copper of high strength is not obtainable. Therefore, as a copper alloy having a tensile strength of 1200 MPa, there was no copper alloy other than beryllium copper, which monopolized the market.

[0012] However, beryllium copper is not an ideal copper alloy; it is inferior to titanium copper in stress relief characteristics, and is not fully satisfactory. Therefore, in a titanium copper alloy containing Ti at 2.0 to 3.5% by mass, if the tensile strength could be improved to 1200 MPa or more, the alloy would be an optimal high strength copper alloy having the stress relief characteristics, and hence improvement is anticipated.

#### SUMMARY OF THE INVENTION

[0013] The invention is made in light of above circumstances, and it is hence an object thereof to provide a titanium copper alloy as a terminal connector material which is enhanced in strength without having lowered bending properties. It is also an object of the invention to provide a high

strength titanium copper alloy having a tensile strength of 1200 MPa or more, equivalent to that of beryllium copper, and an electrical conductivity of 10% IACS or more, a manufacturing method thereof, and an electronic component using the same high strength titanium copper alloy, in particular, a fork-shaped connector.

[0014] The inventors attempted to adjust conditions of the final recrystallization annealing of titanium copper alloy (conditions of solution treatment), and the subsequent cold rolling and aging conditions, researched the relationship between characteristic values after final heat treatment, and discovered that a titanium copper alloy material enhanced in strength without having lowered bending properties can be obtained stably. [0015] The present invention is made on the basis of the above knowledge. A first aspect of the present invention provides a high strength titanium copper alloy consisting of Ti at 2.0% by mass or more to 3.5% by mass or less; the balance of copper and inevitable impurities; and an average grain size of  $20~\mu m$  or less; the alloy further comprising a 0.2% proof stress expressed by "b" of  $800~N/mm^2$  or more; and a bending radius ratio (bending radius/sheet thickness) not causing cracking as expressed by "a" by a W-bending test in a transverse direction to a rolling direction; wherein "a" and "b" satisfy a  $\leq 0.05 xb - 40$ .

[0016] The second aspect of the invention provides a high strength titanium copper alloy consisting of Ti at 2.0% by mass or more to 3.5% by mass or less; at least one of Zn, Cr, Zr, Fe, Ni, Sn, In, Mn, P, and Si at 0.01% by mass or more to 3.0% by mass or less in total; and the balance of copper and inevitable impurities; the alloy further comprising an average grain size of  $20~\mu m$  or less; a 0.2% proof stress expressed by "b" of 800 N/mm² or more; and a bending radius ratio (bending radius/sheet thickness)

not causing cracking as expressed by "a" by a W-bending test in a transverse direction to a rolling direction; wherein "a" and "b" satisfy  $a \le 0.05xb - 40$ .

[0017] The reasons for setting the numerical values specified above are explained below together with the operation of the invention. In the following explanation, "%" means "% by mass."

A. Ti: 2.0 to 3.5%

[0018] Ti is characterized by inducing spinodal decomposition by aging of Cu-Ti alloy, thereby generating a concentration modulation structure in the matrix, and assuring a very high strength. However, desired reinforcement is not expected if the content is less than 2.0%. If Ti is contained at more than 3.5%, precipitation of grain boundary reaction type is likely to occur, and the strength may be lowered, in contrast, and the workability deteriorates. Hence, the content of Ti is defined in a range of 2.0 to 3.5%.

B. Zn, Cr, Zr, Fe, Ni, Sn, In, Mn, P, Si: 0.01 to 3.0% in total [0019] Cr, Zr, Fe, Ni, Sn, In, Mn, P, and Si are all known to suppress precipitation of grain boundary reaction type without substantially lowering the electrical conductivity of a Cu-Ti alloy, make grain size fine, and increase the strength by aging precipitation. Moreover, Sn, In, Mn, P, and Si are known to increase the strength of a Cu-Ti alloy by solid solution reinforcement. Therefore, one or more elements thereof are added as required. However, if the total content thereof is less than 0.01%, desired effects are not expected. If the total content exceeds 3.0%, the electrical conductivity and workability of the Cu-Ti alloy deteriorate significantly. Therefore, the content of one element or more elements of Zn, Cr, Zr, Fe, Ni, Sn, In, Mn, P, and Si is specified to be in a range of 0.01 to 3.0% in

total.

[0020] Of these additive elements, Zn is expected to suppress heat peel off of solder without lowering the electrical conductivity of a Cu-Ti alloy, and is added most preferably. However, if the content of Zn is less than 0.05%, desired effects are not expected. If the content of Zn exceeds 2.0%, the electrical conductivity and stress relief characteristics deteriorate.

Therefore, the content of Zn is preferred to be in a range of 0.05 to 2.0%.

C. Characteristics of titanium copper alloy

[0021] In order that a titanium copper alloy be used as a terminal connector material, in particular, the bending properties are important because it is used being formed into a complicated part, together with its material strength. In the designing of a part, considerations are given to the 0.2% proof stress as the index of material strength, and the bending properties evaluated by the state of the bending part when it is bent at various bending radii with respect to the material plate thickness. The inventors quantitatively analyzed the bending properties depending on the strength and plate thickness required in the recent electronic components, and discovered a specific scale balancing both as explained below. [0022] That is, when the 0.2% proof stress expressed by "b" is 800 N/mm<sup>2</sup> or more, the bending radius ratio (bending radius/sheet thickness) not causing cracking as expressed by "a" by a W-bending test in a transverse direction to a rolling direction, "a" and "b" satisfy  $a \le 0.05xb$  – 40, the high strength and bending properties can be balanced, and the titanium copper alloy can meet recent demands. The 0.2% proof stress of titanium copper alloy is defined to be 800 N/mm<sup>2</sup> or more because the high strength characteristics as a titanium copper alloy cannot be exhibited sufficiently if less than 800 N/mm<sup>2</sup>. In the invention, the grain size is

shown in Fig. 1.

measured by using the value obtained by the cutting method according to IIS H 0501.

[0023] To enhance the strength of titanium copper alloy, it has been known to reinforce the solid solution by adding alloy elements, reinforce precipitation by adequately controlling the aging temperature, or reinforce by work hardening by adequately controlling the working ratio before aging, and hitherto the desired material characteristics were assured by combining these methods. However, when the strength is enhanced by such reinforcing mechanisms only, the bending properties may deteriorate, and it may fail to reach a desired region of material characteristics. Accordingly, the inventors conducted various tests, and found that there is a relationship between the strength and bending properties with respect to the grain size, and that the average grain size of 20 µm is required in order to obtain the above relationship of 0.2% proof stress and bending radius ratio. [0024] Furthermore, in order to enhance the bending properties without lowering the material strength, it is necessary to define the grain size strictly, and to control adequately the final recrystallization annealing condition, cold working ratio, and aging temperature. The invention also provides a terminal connector using such titanium copper alloy. [0025] The manufacturing method for titanium copper alloy of the invention is characterized by performing final recrystallization annealing at a temperature below the borderline L of the α-phase and the α+Cu<sub>3</sub>Ti phase

[0026] It is essential in the invention to specify the final recrystallization annealing condition, and the subsequent cold working and aging conditions. The final recrystallization annealing condition is intended to facilitate the subsequent process, and to adjust the material characteristics and grain size.

to  $20 \mu m$ .

[0027] Hitherto, to manufacture a titanium copper alloy of which the grain size does not exceed 20  $\mu$ m, the grain size was adjusted by adequately controlling the treatment time by determining the treating temperature in a solid solution region of Ti. However, in the case of recrystallization by solution treatment at high temperature and in a short time, since the uniformity of grain size is insufficient, although the strength may be enhanced, the workability is impaired, the characteristics vary widely, and hence it was difficult to stabilize the high strength of titanium copper alloy at a grain size of 20  $\mu$ m or less.

[0028] Accordingly, the inventors made various tests about recrystallization annealing, and discovered that a titanium copper alloy superior in bending properties without lowering the strength and having small variations of characteristics can be obtained, in each composition, by performing recrystallization annealing at a temperature below the borderline L of  $\alpha$ -( $\alpha$ +Cu<sub>3</sub>Ti) which is the borderline of the solid solution-precipitation, that is, in a temperature region partially causing precipitation, instead of temperature region of solid solution of all contained Ti in Cu, for a time so that the average grain size does not exceed  $20~\mu m$ . The temperature y (°C) of  $\alpha$ -( $\alpha$ +Cu<sub>3</sub>Ti) borderline L can be approximated in formula y = 50x + 650, where x (%) is the concentration of Ti. [0029] Meanwhile, as the grain size becomes finer, the bending properties are better, but if the average grain size is less than  $3~\mu m$ , non-recrystallized

[0030] The cooling rate after recrystallization annealing should be 100°C/sec or more. If the cooling rate is less than 100°C/sec, spinodal

portion may remain, and the bending properties may deteriorate, and therefore the average grain size should be  $20 \mu m$  or less, more preferably 3

decomposition occurs at the time of cooling, and the material is hardened, and the subsequent working becomes difficult. It is hence preferred to cool the material surface coming out of the heating furnace by water or steam and water, so that the material can be cooled uniformly while maintaining the specified cooling rate.

[0031] Furthermore, in order to obtain such characteristics correlation of 0.2% proof stress and bending properties, aside from the recrystallization annealing condition, it is required to specify the subsequent cold working ratio and aging condition strictly. After recrystallization annealing, almost all Ti of the material is in solid solution, and then it is worked by cold rolling and aged. The working ratio of cold rolling is preferred to be 5 to 70% or less. If it is less than 5%, increase in strength by work hardening is small, and desired strength is not obtained, but when the working ratio exceeds 70%, although a high strength is obtained by adequately controlling the aging condition, the bending properties deteriorate, and the correlation of 0.2% proof stress and bending properties are not obtained. [0032] The aging condition is preferred to be 300°C or more to 600°C or less. If the aging temperature is less than 300°C, aging is not sufficient. and the material strength is not improved. If it is aged at a temperature over 600°C, the solid solution amount of Ti is excessive (the precipitation amount is less), and desired strength is not obtained. The period of aging is preferred to be 1 hour or more to 15 hours or less. If it is less than 1 hour, improvement of strength and electrical conductivity by aging is not expected, or if it exceeds 15 hours, the strength declines due to over-aging. [0033] Accordingly, the titanium copper alloy of the invention is an aging-cured type copper alloy of superior bending properties and high strength, and it is used in the terminal connector of small size in which

superior bending properties and high strength are required. If the contact of the terminal connector is plated before or after press working, the strength and bending properties hardly deteriorate, and the effect of the invention is exhibited.

[0034] Such high strength titanium is generally press worked after the aging process. The inventors discovered that the bending properties are further enhanced by limiting the range of grain size in further narrower bounds while aging after pressing process. That is, the invention according to a third aspect provides a titanium copper alloy which is subjected to an aging process after press working, the alloy consisting of: Ti at 2.0% by mass or more to 3.5% by mass or less; and the balance of copper and inevitable impurities; the alloy further comprising a grain size of 5 to 15  $\mu$ m; wherein cracking does not occur by a W-bending test in a transverse direction to a rolling direction with a bending radius of zero before the aging process, and the hardness of the worked matrix after the aging process is 300 Hv or more, and it is more preferable that it be 310 Hv or more.

[0035] Moreover, the invention according to a fourth aspect provides a titanium copper alloy which is subjected to an aging process after press working, the alloy consisting of: Ti at 2.0% by mass or more to 3.5% by mass or less; at least one of Zn, Cr, Zr, Fe, Ni, Sn, In, Mn, P, and Si at 0.01% by mass or more to 3.0% by mass or less in total; and the balance of copper and inevitable impurities; the alloy further comprising a grain size of 5 to 15  $\mu$ m; wherein cracking does not occur by a W-bending test in a transverse direction to a rolling direction with a bending radius of zero before the aging process, and the hardness of the worked matrix after the aging process is 300 Hy or more, and it is more preferable that it be 310 Hy

or more.

[0036] Such high strength titanium copper alloy is manufactured by performing final recrystallization annealing at a temperature below the borderline of  $\alpha$ -phase and  $\alpha$ +Cu<sub>3</sub>Ti phase to adjust the grain size to 5 to 15  $\mu$ m, and executing final cold rolling at a working ratio of 5 to 50%. The aging conditions may be the same as in the first and second aspects of the invention, and such a manufacturing method is also one of the features of the invention. Furthermore, the third and fourth aspects are also applied in the terminal connector of small size where superior bending properties and high strength are required, and such a terminal connector is also one of the features of the invention.

[0037] The inventors further researched the manufacturing process of titanium copper alloy, and adjusted the hot rolling condition, and the subsequent cold rolling condition and aging condition, and discovered that a high strength titanium copper alloy having a tensile strength of 1200 MPa or more can be obtained stably.

[0038] That is, a fifth aspect of the invention provides a high strength titanium copper alloy consisting of: Ti at 2.0% by mass or more to 3.5% by mass or less; and the balance of copper and inevitable impurities; the alloy further comprising a tensile strength of 1200 MPa or more and an electrical conductivity of 10% IACS or more.

[0039] The sixth aspect of the invention provides a high strength titanium copper alloy consisting of: Ti at 2.0% by mass or more to 3.5% by mass or less; Zn at 0.05% by mass or more to 2.0% by mass or less; at least one of Cr, Zr, Fe, Ni, Sn, In, Mn, P, and Si at 0.01% by mass or more to 3.0% by mass or less in total; and the balance of copper and inevitable impurities; the alloy further comprising a tensile strength of 1200 MPa or more and an

electrical conductivity of 10% IACS or more.

[0040] The high strength titanium copper alloy can be manufactured by hot rolling at a temperature of 600°C or more, cold rolling successively at a working ratio of 95% or more, and aging at temperature of 340°C or more to less than 480°C for 1 hour or more to less than 15 hours while maintaining the state of the matrix after cold rolling.

[0041] The invention further provides a fork-shaped connector using the high strength titanium copper alloy of the fifth or sixth aspect.

[0042] In the fifth and sixth aspects, the reasons for limiting the contents are the same as in the first and second aspects. The reasons for limiting the characteristic values in the fifth and sixth aspects are as follows.

#### (1) Tensile strength

[0043] The fork-shaped connector for FPC differs from the general-purpose connector contacting with the surface of metal material, is designed to contact with the circuit board at the fracture of copper alloy plate, and is not processed by bending. Accordingly, the requirement of prime importance is the strength. In the invention, the strength is evaluated by tensile strength. The required tensile strength of a fork-shaped connector is not sufficient at the tensile strength obtained by general-purpose copper alloy such as brass, phosphor bronze, or nickel silver, but is 1200 MPa or more so as to be applicable to versatile designs as fork-shaped connectors.

# (2) Electrical conductivity

[0044] As the metal material for fork-shaped connector for FPC, the strength is most important, but since the fork-shaped connector is designed to contact at the fracture of metal material, the contact resistance is larger than in other connectors. As a countermeasure, the contact area is plated

with gold, but certain electrical conductivity is also required as metal material. Some stainless steel materials are high in strength, but the electrical conductivity is low, and the heat generated in the contact portion is poorly dissipated. At least, an electrical conductivity of 10% IACS is needed.

[0045] The high strength titanium copper alloy of the fifth and sixth aspects is manufactured in the following method.

[0046] Hitherto, in the manufacturing method for enhancing the strength of titanium copper alloy, after hot rolling, cold rolling and heat treatment, the material is heated (solution treatment) to adjust the grain size at 20  $\mu$ m or less, and the working ratio of final cold rolling and aging temperature are properly controlled, so that a material of tensile strength of about 1000 MPa and superior bending property is manufactured (Japanese Patent Application Laid-Open No. 7-258803). However, considering the manufacturing efficiency, in the Ti amount range of 2.0 to 3.5% by mass, the tensile strength of 1200 MPa or more is not yet achieved in the high strength titanium copper alloy manufactured in this method. As for the MTH treatment mentioned above, the tensile strength of 1200 MPa or more is not yet obtained in the Ti amount range of 2.0 to 3.5% by mass.

[0047] In the manufacturing method of the invention, it is essential to specify the "material temperature in hot rolling," "working ratio in cold rolling before aging process," and "aging condition."

# (1) Hot rolling

[0048] Hot rolling is intended to homogenize the cast matrix, and to induce dynamic recrystallization by rolling at higher temperature, so that subsequent processes can be easily performed. If the material temperature is lower than 600°C during hot rolling, titanium copper alloy causes

spinodal decomposition to harden abruptly, and the subsequent cold working is difficult, and the characteristics vary widely. Therefore, the material temperature is kept above 600°C during the hot rolling process. As for cooling after hot rolling, the material hardness unless cooled quickly and the subsequent rolling is difficult, and therefore, by water cooling or the like, the cooling rate of the material is preferred to be 200°C/sec or more.

### (2) Cold rolling

[0049] So far, the titanium copper alloy was cold rolled and annealed after the hot rolling process, and then cold rolled to a specified sheet thickness, and was further heated (solution treatment) for a short time at a high temperature before aging process. That is, heat treatment is intended to adjust the material characteristics and to make the subsequent processing easier, but since the heat treatment is applied between the hot rolling and the aging, a proper working ratio of cold rolling cannot be set, the strength is lowered, and it is hard to obtain a desired high strength.

[0050] However, by strictly specifying the working condition of hot rolling, a strong working of 95% or more is possible in the subsequent cold rolling. Herein, the working ratio of cold rolling is 95% or more because the working ratio must be specified strictly in order to obtain a tensile strength of 1200 MPa or more by the subsequent aging process, although the strength is generally elevated as the working ratio is higher, and a tensile strength of 1200 MPa or more can be obtained by defining the working ratio at 95% or more.

# (3) Aging

[0051] After the cold rolling process, the material is aged in order to reinforce the strength and improve the elongation, elastic property and electrical conductivity. The aging temperature is defined in a range of 340°C to less than 480°C, that is, if the aging temperature is less than 340°C, the aging effect is not sufficient, and the strength and electrical conductivity are not improved, but at 480°C or more, since the cold rolling working ratio before aging process is strong working of 95% or more, it may result in over-aging if aged for a short time, and the strength is lowered and desired characteristics are not obtained, and therefore the temperature range of 340°C or more to less than 480°C is specified.

[0052] The aging period is 1 hour or more to less than 15 hours, that is, if less than 1 hour, improvement of strength and electrical conductivity by aging is not expected, and if 15 hours or more, the strength is lowered due to excessive over-aging, and hence the aging period is defined in a range of 1 hour or more to less than 15 hours.

[0053] Such high strength titanium copper is generally press worked after the aging process. The inventors discovered that dimensional changes after aging are substantially small. Therefore, the invention according to a seventh aspect provides to a titanium copper alloy which is subjected to an aging process after press working, the alloy consisting of: Ti at 2.0% by mass or more to 3.5% by mass or less; and the balance of copper and inevitable impurities; the alloy further comprising a worked matrix having a hardness of 345 Hv or more after the aging process.

[0054] Furthermore, an eighth aspect of the invention provides a titanium copper alloy which is subjected to an aging process after press working, the alloy consisting of: Ti at 2.0% by mass or more to 3.5% by mass or less; Zn at 0.05% by mass or more to 2.0% by mass or less; at least one of Cr, Zr, Fe, Ni, Sn, In, Mn, P, and Si at 0.01% by mass or more to 3.0% by mass or less in total; and the balance of copper and inevitable impurities;

the alloy further comprising a worked matrix having a hardness of 345 Hv or more after the aging process.

[0055] The high strength titanium copper alloys of the seventh and eighth aspects are manufactured by hot rolling at a temperature of 600°C or more, and cold rolling successively at a working ratio of 95% or more, and such a manufacturing method is also one of the features of the invention. The high strength titanium copper alloys of the seventh and eighth aspects are particularly suited to a fork-shaped connector, and such a fork-shaped connector is also one of the features of the invention.

#### BRIEF DESCRIPTION OF DRAWING

[0056] Fig. 1 is a Ti-Cu equilibrium diagram.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

Examples

(Example 1)

[0057] The invention is specifically explained below by referring to example 1 which shows a particularly preferred alloy composition range. First, using electrolytic cathode copper or oxygen-free copper as a raw material, copper alloy ingots (50 mm thick x 100 mm wide x 200 mm long) of various compositions shown in Table 1 (examples) and Table 2 (comparative examples) were melted in a high frequency melting furnace. Consequently, each ingot was heated for 1 hour at a temperature of 850 to 950°C, and was hot rolled, and a plate with 8 mm thick was obtained. At this time, the material temperature after hot rolling was 650°C or more, and the material was cooled in water after hot rolling. The oxide layer on the surface of the sheet was polished and removed, and rolling and

recrystallization annealing were repeated, and after proper pickling, recrystallization annealing (solution treatment) was conducted in the condition of Tables 1 and 2, being followed by cold rolling and aging, and a material having a thickness of 0.2 mm was obtained. After recrystallization annealing, the material was cooled by immersing in water after heat treatment. At this time, the cooling rate was 200°C/sec or more, which was confirmed by attaching a thermocouple to the material surface. The table also records the value of temperature of  $\alpha$ -( $\alpha$ +Cu<sub>3</sub>Ti) borderline as approximated in formula (y = 50x + 650). As shown in Table 1, in the invention, recrystallization annealing was conducted at a temperature below the  $\alpha$ -( $\alpha$ +Cu<sub>3</sub>Ti) borderline and within 50°C. [0058]

Table 1

	Compositi	Composition (unit: % by mass)			Manufacturi	Manufacturing conditions		
Š			Temperature at	Recrystalli	Recrystallization annealing condition		Aging condition	ition
	E	Others	α-(α+Cu <sub>3</sub> Π) borderline (C)	Temperature (C)	Average crystal particle size ( $\mu$ m)	processing ratio (%)	Heating temperature (C)	Holding time (hours)
	3.2		810	770	10	20	380	9
2	2.9		795	750	2	40	400	9
3	5.6	,	780	750	5	40	420	9
4	2.4		770	750	2	40	420	9
5	3.5		825	170	10	20	400	9
9	3.0		800	770	10	20	400	9
7	2.9	Zn1.0	795	750	10	20	380	10
	2.2	Sn0.21	160	750	10	30	380	10
6	2.5	Cr0.10	775	750	10	65	380	9
01	3.0	Zr0.15	800	770	10	09	380	9
11	3.2	Fe0.20	810	750	2	20	400	9
2	2.7	Ni0.30	785	750	10	20	380	9
13	3.2	In0.25	810	770	20	40	420	9
14	3.0	Mn0.10	800	750	10	20	380	10
2	3.1	P0.07	802	750	10	50	400	10
16	2.8	Si0.13	790	750	10	30	380	9
17	2.7	Zn0.70, Cr0.30, Zr0.15	785	750	2	09	380	9
82	2.7	Zn0.50, Fe0.15, P0.05	785	750	10	09	420	9
61	2.9	Zn1.2, ln0.10, Fe0.16, P0.03	795	750	5	30	420	9
20	3.1	Sn0.15, P0.15	802	770	10	50	400	9
21	2.6	Mn0.15, Po.10	780	750	10	60	380	9
22	2.9	Zn0.80, Ni0.25, Si0.05	795	750	01	09	380	9
23	3.3	Zn1.1, Cr0.15, Zr0.05, Mn0.05	815	770	10	09	380	9
24	3.2	Zn0.1, Ni0.25,	810	770	01	09	380	9

[0059]

# Table 2

Wa
Recrystall Temperature
છ
989
200
770
770
750
750
810
850
750
750
750
720
7.70
220
750

[0060] From these materials obtained by such series of processing, various test pieces were sampled, and the characteristics thereof were tested. First, to evaluate the elastic properties and strength, tensile tests were conducted, and 0.2% proof stress, tensile strength and elongation were measured according to JIS Z 2201 and Z 2241. As for bending properties, test pieces measuring 10 mm wide x 100 mm long were sampled at the transverse angle to the rolling direction, and W-bending tests (JIS H 3110) were conducted at various bending radii, and the minimum bending radius ratio (r/t, r: bending radius, t: test piece thickness (sheet thickness)), not causing cracking, capable of obtaining a favorable bend appearance of rank C or higher in the evaluation standard according to Japan Brass Technical Association standard JBTA T307: 1999 was determined by observing the bend with an optical microscope. This evaluation standard is classified in five ranks; rank A: no wrinkle, rank B: small wrinkle, rank C: large wrinkle, rank D: small crack, and rank E: large crack, and in the case of bending test at larger bending radius ratio than the bending radius ratio for obtaining the result of rank C, appearance of the same or better ranks A to C is obtained. In W-bending test, the bending axis is parallel (Bad Way) to the rolling direction in which the bending properties are inferior. The bending radius is the distance from the center of bending to the inner circumference of the test piece, and the results were evaluated by using a tool having various bending radii.

[0061] Results of characteristic tests are shown in Table 3 (examples) and Table 4 (comparative examples). In examples No. 1 to No. 24, the bending radius ratio (bending radius/sheet thickness) not causing crack as expressed by "a" and 0.2% proof stress expressed by "b", and "a" and "b"

satisfy the relationship "a  $\leq 0.05$ xb -40", and the titanium copper alloy (evaluation: favorable) meeting the recent demands, and well-balanced between high strength and bending properties, could be obtained. In contrast, in comparative examples No. 25 to No. 39, as explained below, the requirements of the invention were not satisfied, and poor bending properties and other problems were found at 0.2% proof stress.

proof stress of 800 N/mm<sup>2</sup> or more is not obtained. In No. 27 and 28, the strength is lower than in the alloy of the example of the invention, and the bending radius ratio is large, and the bending properties are poor. This is because the Ti content is too high, and there is too much precipitation into the grain boundary not contributing to enhancement of strength, and it seems cracks are initiated from the precipitates in the grain boundary at the time of performing tension tests and bending tests.

[0062] In No. 25 and 26, since the Ti content is low, high strength of 0.2%

[0063] No. 29 has too high amount of Zn, and No. 30 has too high a total amount of subsidiary additives, and they are both low in electrical conductivity and poor in bending properties. No. 31 and 32 are examples of extremely high recrystallization temperature, in which average grain size of  $20~\mu m$  or less was not obtained, and high 0.2% proof stress could not be obtained. When compared with an alloy example of 0.2% proof stress of the same level in the invention, the bending radius ratio is large and bending properties are poor. No. 31 is a mixed grain matrix.

Accordingly, the average grain size in No. 31 is 25  $\mu$ m, being smaller than in No. 32, but the bending radius ratio varied in a range of 3.0 to 5.0. The maximum value is recorded in Table 4.

[0064] No. 33 and 34 are examples of too high working ratio of cold rolling, but by shortening the aging period, a high 0.2% proof stress was

obtained, however, the bending properties were poor. No. 35 is an example of low aging temperature, and since the temperature is low, the aging effect is insufficient, and the strength is low. No. 36 is an example of too long aging period, and 0.2% proof stress is lowered due to overaging.

[0065] No. 37 is an example of too high aging temperature and too short aging period, and since the aging temperature is too high, the solid solution amount of Ti is excessive, and since the aging period is short, sufficient 0.2% proof stress is not obtained. No. 38 is an example of short aging period, and the aging effect is insufficient, and the 0.2% proof stress is low. No. 39 is an example of low aging temperature, and in spite of long aging period of 50 hours, high 0.2% proof stress is not obtained. [0066] Therefore, in the alloy examples of the invention, by recrystallization annealing (solution treatment) at a temperature below the  $\alpha$ -( $\alpha$ +Cu<sub>3</sub>Ti) borderline in an appropriate composition, and performing the subsequent cold rolling and aging process in adequate conditions, a favorable relation of 0.2% proof stress and bending radius ratio is obtained, and titanium copper alloy of high strength is obtained without sacrificing

the bending properties. In contrast, in alloys of comparative examples, as compared with alloys of the invention, favorable relation of 0.2% proof stress and bending radius ratio is not obtained, and material with good

[0067]

balance is not produced.

Table 3

	Tensile	0.2% proof	Elongation	0.05 x b-40	Bending radius	Electrical
No.	strength	stress (b)		0.00 X D-40	(r / t)	Conductivity
		1	(%)			m. 7.4.000
- 1	(N/mm <sup>2</sup> )	(N/mm <sup>2</sup> )				(%IACS)
1	1050	900	15	5.0	3.0	14.4
2	1030	880	17	4.0	2.0	14.3
3	1030	900	15	5.0	2.0	14.1
4	1020	900	16	5.0	2.0	14.3
5	1050	940	15	7.0	3.0	13.6
6	1070	960	14	8.0	3.0	13.2
7	1030	890	17	4.5	3.0	14.2
8	880	830	23	1.5	1.0	15.3
9	970	880	18	4.0	8.0	13.4
10	1010	900	17	5.0	3.0	14.5
11	1060	920	17	6.0	3.0	
12	1030	910	15	5.5	3.0	14.5
13	1070	930	10	6.5	4.0	13.4
14	1040	910	15	5.5	3.0	13.4
15	1040	920	14	6.0	3.0	13.7
16	950	850	20	2.5	0.0	13.5
17	1110	950	8	7.5	4.0	14.7
18	1010	900	14	5.0	3.0	14.0
19	970	860	18	3.0	1.0	15.1
20	1060	940	10	7.0	3.0	14.0
21	990	900	12	5.0	4.0	14.4
22	1050	930	11	6.5	3.0	13.7
23	1080	990	8	9.5	4.0	14.7
24	1040	930	11	6.5	4.0	14.6

[0068]

Table 4

No.	Tensile strength (N/mm²)	0.2% proof stress (b) (N/mm²)	Elongation	0.05 x b-40	Bending radius ratio (r / t)	Electrical Conductivity (%IACS)
		600	11		5.0	35.0
25	680		8		5.0	20.3
26	790	710	1	<del> </del>	8.0	10.4
27	750	720	1 2		7.0	10.3
28	800	750		3.0	5.0	8.3
29	960	860	8		5.0	7.1
30	950	840	10	2.0	5.0	14.3
31	850	760	25	<u> </u>		14.4
32	880	800	20	0.0	4.0	15.3
33	1150	970	10	8.5	>10.0	15.1
34	1180	990	15	9.5	>10.0	
35	820	750	3		3.0	12.1
	890	780	20		3.0	15.2
36		720	18		1.0	15.1
37	800	760	7		4.0	12.3
38	850		7	<del></del>	3.0	12.4
39	820	750	1			

# (Example 2)

[0069] Test pieces were press worked at the process conducted up to cold rolling in the same condition as in examples No. 2 and No. 10 in example 1 except that the final recrystallization annealing was conducted in the conditions as shown in Table 5. The press worked test pieces were evaluated by W-bending test in the same condition as in example 1, and then were subjected to aging. The aging conditions were  $400^{\circ}$ C and 6 hours in No. 2, and  $380^{\circ}$ C and 6 hours in No. 10. Before and after the aging process, characteristics of test pieces were examined using the same method as in example 1, and the results are shown in Table 5. As is clear from Table 5, when the average grain size is in a range of 5 to  $15 \,\mu\text{m}$ , the bending radius ratio (r/t) is zero, and an extremely superior bending properties were confirmed. In these test pieces, the hardness after aging process was 310 Hv or more, and the tensile strength was  $1000 \, \text{MPa}$  or more.

[0070]

# Table 5

Machine	- 1								,		Charac	Characteristics after aging process	aging process		
Carbonium   Carb			Recrysta	lization	Average	Ö	haracteristic be	fore aging proce	2		0.2%				Evaluation
750         80         7         70         70         70         10         137         300         10           750         30         3         8         1         3         2         4         0         1030         850         17         143         310         80         1         143         310         80         1         143         310         80         1         143         310         80         1         143         310         80         1         143         310         80         1         143         310         80         1         143         310         80         1         143         310         80         1         141         310         80         1         141         310         80         1         141         310         80         1         141         310         80         1         141         310         80         1         86         1         141         310         1         141         310         1         141         310         310         1         141         310         310         310         310         310         310         310         310 <td< td=""><td>ā</td><td>nposition wt%</td><td>ړ</td><td>Holding</td><td>crystal particle</td><td>Tensile strength</td><td>Elongation</td><td>Electrical Conductivity</td><td>MBR/I</td><td>Tensile strength MPa</td><td>proof</td><td>Elongation %</td><td>Conductivity %IACS</td><td>Hardness Hv</td><td></td></td<>	ā	nposition wt%	ړ	Holding	crystal particle	Tensile strength	Elongation	Electrical Conductivity	MBR/I	Tensile strength MPa	proof	Elongation %	Conductivity %IACS	Hardness Hv	
750         30         3         850         1         3         6         100         100         850         17         143         315         5           750         40         10         10         10         10         10         10         12.6         315         315         31         <	- 1			sec.		Mra	88			970	900	01	13.7	300	Bending inferior
750         45         5         790         2         4         0         100         550         12.5         3290         5           750         80         10         770         2         4         0         1035         950         13         13.5         310         55           750         10         170         2         4         0         1035         950         13         14.1         315         310         55           750         150         150         150         950         14         9.5         110         31         310         31 </td <td>~</td> <td>PTI-Cu</td> <td>750</td> <td>90</td> <td>က</td> <td>820</td> <td>-</td> <td>0</td> <td>,</td> <td></td> <td>000</td> <td>1.7</td> <td>14.3</td> <td>315</td> <td>Superior</td>	~	PTI-Cu	750	90	က	820	-	0	,		000	1.7	14.3	315	Superior
750         60         8         755         2         4         0         1030         570         137         310         S           750         180         10         170         2         4         0         1030         920         13         141         310         S           750         180         20         670         1         6         1030         920         13         141         310         S           770         180         20         670         1         6         2         2         97         160         137         300         10           770         40         5         780         1         2         2         864         14         142         310         300         10           770         40         5         780         2         3         0         1018         920         15         142         310         310           770         40         5         780         2         3         0         1010         900         17         144         310           770         120         10         10         10         90 <td>1</td> <td>0</td> <td>036</td> <td>A.F.</td> <td>15</td> <td>790</td> <td>2</td> <td>4</td> <td>0</td> <td>1030</td> <td>000</td> <td>10</td> <td>19.5</td> <td>320</td> <td>Superior</td>	1	0	036	A.F.	15	790	2	4	0	1030	000	10	19.5	320	Superior
750         89         10         770         2         4         0         1000         3220         13         141         315         S           750         180         15         760         1         6         2         972         854         14         9.5         310         15           750         180         26         2         972         854         14         9.5         310         1           770         20         3         820         1         2         2         980         870         10         13.7         300         1           770         40         5         780         2         3         0         1015         920         15         14.2         310         30           770         40         5         780         2         3         0         1015         940         15         14.2         310         315 <td>1</td> <td>2.911-Cu</td> <td>000</td> <td>3</td> <td></td> <td>785</td> <td>2</td> <td>4</td> <td>0</td> <td>1035</td> <td>040</td> <td>2 5</td> <td>13.7</td> <td>310</td> <td>Superior</td>	1	2.911-Cu	000	3		785	2	4	0	1035	040	2 5	13.7	310	Superior
750         100         15         760         1         4         0         1000         322         854         14         95         310         1           750         180         20         670         1         5         2         2         854         14         95         310         1           770         180         20         670         1         5         2         2         2         860         870         10         13.7         300         1           770         40         5         780         2         3         0         1015         940         15         14.2         310         3           770         40         5         780         2         3         0         100         90         17         14.4         310           770         10         2         3         0         1010         90         17         14.4         310           770         10         10         10         30         10         14.4         310         310           770         10         20         60         10         2         90         17	1	2-11-Cu	026	8 8	9	770	2	4	0	1030	926	100	14.1	315	Superior
750         180         20         670         1         5         2         972         854         14         2.5         2.5         854         14         2.5         2.5         854         14         2.5         2.5         854         14         2.5         2.5         2.5         850         870         10         13.7         300         13.7         300         13.7         300         13.7         300         13.7         300         13.7         310         300         13.7         310	1	2011-01	750	120	15	760	-	4	•	1020	920	:	40	310	Bending
770         20         3         820         1         2         2         980         870         10         137         300           770         40         5         780         2         3         0         1015         920         15         142         310         310           770         60         8         770         2         3         0         1020         940         15         143         316           770         80         10         780         2         3         0         1010         960         17         144         310           770         120         15         15         760         1         3         0         1015         960         17         144         310           770         150         20         1         3         0         1015         990         15         140         300           770         150         20         1         4         2         990         80         1         140         300	1	2	750	180	8	670	-	ro.	67	972	824	P1	0:0		Bending
770         20         20         20         3         0         1015         920         15         142         310           770         40         5         780         2         3         0         1020         940         15         139         315           770         80         10         780         2         3         0         1010         900         17         144         310           770         120         15         15         760         1         3         0         1015         900         17         140         310           770         150         20         60         1015         900         17         9.8         300	12	Ti-0 15Zr-		8	1.	88	-	84	2	086	870	01	13.7	300	inferior
770         40         5         780         2         3         0         1020         940         15         139         316           770         60         8         770         2         3         0         1020         940         17         144         310           770         80         10         780         2         3         0         1015         900         17         144         310           770         120         15         760         1         3         0         1015         900         15         140         310           770         150         20         650         1         4         2         990         80         17         9.8         300	: 1	Cn	2	RZ	•					1015	920	15	14.2	310	Superior
770         60         8         770         2         3         0         1020         3+0         1-2         3+0         1020         3+0         1-2         3+0         1020         3+0         1-2         104         310           770         120         15         760         1         3         0         1015         390         15         1440         310           770         150         20         650         1         4         2         390         17         9.8         300	<u>ي</u>	Ti-0.15Zr- Cu	0/1	40	10	780	22	2			3	=	13.9	315	Superior
770         80         10         780         2         3         0         1010         900         17         17.7         120         18         760         1         3         0         1015         900         15         14.0         310           770         150         20         680         1         4         2         990         890         17         9.8         300	18	Ti-0.15Zr-	170	9	80	770	2	8	•	IOZO	940	: :	77	310	Superior
770         120         15         760         1         3         0         1015         900         15         140         310           770         150         25         680         1         4         2         990         890         17         9.8         300	18	Ti-0.15Zr-	5	8	01	780	2	6	0	1010	900	=	200		
770         120         15         760         1         3         0         1.70         890         17         9.8         300           770         150         20         690         1         4         2         990         890         17         9.8         300	. 1	Ç.	2	3	1	1		,		1015	900	12	14.0	310	Superior
770 150 20 690 1 4 2 990 890 1/ 3.0	<u>ج</u>	0Ti-0.15Zr-	770	120	15	260	-	2	-			!	000	300	Bending
	60	0Ti-0.15Zr-	92	150	20	069	-	4	62	066	880	-	9.6		Interior

#### (Example 3)

[0071] Electrolytic cathode copper or oxygen-free copper, and metal lump of additive elements or master alloy were used as raw materials, and copper alloy ingots of various compositions shown in Table 6 (examples) and Table 7 (comparative examples) were melted in a high frequency melting furnace. Hot tops of these ingots (measuring 50 mm thick x 100 mm wide x 150 mm long, weighing about 7000 g) were cut off, and after removing the surface layer, they were heated for 1 hour or more at 850°C, and the material was hot rolled to a thickness of 8 mm while keeping the temperature at 600°C or more, and it was cooled in water. The material temperature in hot rolling was measured by two-color pyrometer preliminarily compensated for temperature. The surface oxide scale was removed by machine polishing in a thickness of about 0.4 mm on one side, and the plate was cold rolled to a specified thickness of less than 0.4 mm (working ratio 95% or more), and the material surface was degreased by an organic solvent such as acetone, and specified aging was processed in a vacuum annealing furnace, and the sample materials were thereby prepared.

# [0072]

Table 6

Composition and manufacturing conditions of high strength titanium copper alloys of the invention

	Com	position (wt%)		Man	ufacturing cond	litions	
No.			Hot rolling	condition	Cold	Aging	process
	Ti	Others	Min,material temperature (°C)	Final thickness (mm)	processing ratio (%)	Temperature (°C)	Holding time (hr)
1	2.3	-	680	8.0	97	380	6
2	2.6	-	700	8.0	98	380	6
3	2.9	· · · · ·	730	8.5	97	380	10
4	3.2		700	8.0	97	380	10
5	3.4	-	710	7.5	97	360	6
6	3.5	-	730	8.0	97	360	6
7	2.9	Zn1.0, Fe0.20	700	8.0	97	400	6
8	2.6	Sn0.21	700	8.5	98	380	6
9	2.5	Cr0.10	710	7.5	96	420	6
10	3.0	Zr0.15	700	7.5	97	380	10
11	3.2	Fe0.20	720	8.0	97	360	8
12	2.7	Ni0.30	700	8.0	97	380	6
13	3.2	In0.25	680	8.0	97	380	6
14	3.0	Mn0.10	700	8.5	96	380	6
15	3.1	P0.07	700	8.5	98	360	8
16	2.8	Si0.13	710	8.0	97	420	6
17	2.7	Zn0.7, Cr0.30, Zr0.15	710	8.0	97	400	6
18	2.9	Zn1.2, In0.10, Fe0.16, P0.03	730	8.0	97	380	6
19	3.1	Sn0.15, P0.15	720	7.5	96	420	6
20	2.6	Mn0.15, P0.10	700	7.5	99	360	4
21	2.9	Zn0.8, Ni0.25, Si0.05	740	8.0	97	360	8
22	3.3	Zn1.1, Cr0.15, Zr0.05, Mn0.05	750	8.0	97	380	10
23	3.2	Zn0.1, Ni0.25, Sn0.15	710	8.0	97	380	6

[0073]

Table 7

Composition and manufacturing conditions of alloys of comparative examples

	Con	position (wt%)		Man	ufacturing cond	itions					
			Hot rolling	condition	Cold	Aging	process				
No.	т	Others	Min. material temperature (°C)	Final thickness (mm)	rolling processing ratio (%)	Temperature	Holding time (hr)				
24	1.5	-	680	8.0	97	420	6				
25	0.009	Zn1.5, Cr0.30, Zr0.15	680	8.0	97	420	6				
26	5.5	Ni0.50, P0.15	720	35	•)(	Cracked during he	ot rolling				
27	4.0	Zn0.5, Ni1.20, Si0.50	720	8,5	*) C	racked during co	ld rolling				
28	2.8	Zn4.2, Ni1.30, Si0.40	700	8.0	96	380	6				
29	3.1	Zn1.5, Ni1.50, Sn1.10, P0.30	700	8.0	96	380	6				
30	3.0		580	25	*)(	Cracked during h					
31	2.9	Zn1.5	580	15		racked during co	ld rolling				
32	3.2	-	700	10	85	360	6				
33	2.7	Zn1.0, In0.30, P0.15	720	10	90	360	6				
34	3.1	Zn1.5, Fe0.35, Mn0.15	700	8.0	97	200	6				
35	3.1	Zn1.8, Sn0.50	700	8.0	96	450	50				
36	3.0		700	8.5	98	650	0.5				
37	2.9		720	8.5	98	450	0.5				
38	2.8	-	750	8.0	96	200	50				
39	2.9	-	730	8.5	97	-	-				
40	3.2	-	700	8.0	97	-	-				

<sup>\*)</sup> Not examined after cracking

[0074] From the sheet obtained in this manufacturing process, various test pieces were sampled, and were subjected to material tests. The strength was evaluated by the tensile test according to JIS Z 2241, and the 0.2% proof stress, tensile strength, and elongation were evaluated. The test pieces were No. 13B type test pieces conforming to JIS Z 2201. The electrical conductivity was measured according to JIS H 0505. Results of measurements are shown in Tables 8 and 9. [0075]

Table 8

Evaluation of high strength titanium copper alloys of the invention

No.	Tensile strength (MPa)	0.2% proof stress (MPa)	Elongation (%)	Electrical Conductivity (%I ACS)	Evaluation
1	1230	1180	3	10.2	Superior
2	1270	1220	3	11.3	Superior
3	1290	1240	2	11.2	Superior
4	1310	1260	2	10.3	Superior
5	1300	1220	2	11.4	Superior
6	1310	1240	2	10.3	Superior
7	1290	1220	3	11.5	Superior
8	1300	1250	3	10.4	Superior
9	1260	1200	4	10.3	Superior
10	1280	1220	3	11.7	Superior
11	1270	1200	2	11.2	Superior
12	1250	1180	4	12.3	Superior
13	1290	1210	3	12.2	Superior
14	1280	1230	3	11.1	Superior
15	1310	1250	2	10.0	Superior
16	1270	1210	3	11.1	Superior
17	1280	1210	3	12.0	Superior
18	1290	1230	2	10.8	Superior
19	1260	1200	4	11.6	Superior
20	1300	1240	3	10.4	Superior
21	1280	1220	3	12.1	Superior
22	1280	1230	2	12.0	Superior
23	1270	1220	2	11.7	Superior

[0076] Table 9

The state of the s	424 2 11	£1
Evaluation of high strength	titanium copper alloys o	or comparative examples

No.	Tensile strength (MPa)	0.2% proof stress (MPa)	Elongation (%)	Electrical Conductivity (%I ACS)	Evaluation
24	780	720	2	26.4	Poor
25	800	720	2	55.1	Poor
26	-	-	-	-	Not evaluated
27	-	-	-	-	Not evaluated
28	1280	1220	1	8.0	Poor
29	1280	1220	1	7.8	Poor
30	-	-	-		Not evaluated
31	-	-	-	-	Not evaluated
32	1160	1090	1	10.3	Poor
33	1180	1100	1	10.1	Poor
34	1210	1100	1	5.7	Poor
35	1040	940	2	13.2	Poor
36	1060	1000	1	13.1	Poor
37	1250	1160	1	8.0	Poor
38	1230	1130	1	5.8	Poor
39	1220	1120	1	6.0	Poor
40	1250	1160	2	5.8	Poor

[0077] All examples of the invention in Table 8 recorded a tensile strength of 1200 MPa or more as required in a fork-shaped connector, and in particular, examples Nos. 4 to 6, 8, 15, and 20 exhibited a tensile strength of 1300 MPa or more. However, in the comparative examples shown in Table 9, No. 26, 27, 30, and 31 cracked during hot or cold rolling, and the manufacturing efficiency was poor, and the characteristics thereof could not be evaluated. That is, No. 26 and 27 were too high in Ti content, and No. 26 cracked in hot rolling, and although hot rolled to a thickness of 35 mm, subsequent processing was not continued. No. 27 did not crack in hot rolling; however, edge cracking occurred in the subsequent cold rolling. No. 30 and 31 were low in aging temperature, and the temperature was below 600°C at a thickness of 25 mm and 15 mm, respectively, and edge cracking occurred in cold rolling after hot rolling.

[0078] No. 24 is low in Ti content, and it is hence low in strength. No. 25 is also low in Ti content, and it is an example of a Cu-Cr-Zr copper alloy, and although the electrical conductivity is high, the strength is low. No.

28 and 29 are high in contents of Zn and others, and the electrical conductivity is low, and No. 29 formed edge cracking during cold rolling. [0079] No. 32 and 33 are too low in workability of cold rolling, and the strength is low. No. 34 and 38 are low in aging temperature, and in spite of a long aging period of 50 hours for No. 38, desired electrical conductivity is not achieved. No. 37 has a short aging period, and desired electrical conductivity is not achieved. Nos. 35 and 36 are high in aging temperature or have long aging periods, and also because the working ratio of cold rolling before the aging process is high, it results in over-aging, and high strength is not obtained.

[0080] Nos. 39 and 40 are similar to alloys of Nos. 3 and 4 of the invention manufactured in the same process up to cold rolling, but are not aged, and although a high strength of 1200 MPa or more is obtained by cold rolling at high working ratio, the electrical conductivity is low, and they cannot be used in fork-shaped connector.

[0081] Thus, the titanium copper of the invention can be obtained only by the manufacturing method of the invention, and it is a titanium copper alloy having a tensile strength of 1200 MPa or more and an electrical conductivity of 10% IACS or more, not obtainable in the conventional art. The fork-shaped connector using the high strength titanium copper of the invention has a contact pressure equivalent to that of beryllium copper. (Example 4)

[0082] Of the materials manufactured up to the cold rolling processing in Table 6 in example 3, those listed in Table 10 were selected and press worked. These press worked test pieces were aged in the same condition as in example 3. Characteristics of test pieces were investigated before and after the aging process in the same method as in example 3, and the

results are recorded in Table 10. To evaluate the thermal expansion and shrinkage rate, a test piece of 100 mm x 10 mm was cut out in a parallel direction to rolling direction, the distance between specified marking positions was measured by using a three-dimensional coordinate measuring apparatus, and the marking position distance was measured again after the aging process, and the dimension change rate was determined from the measurements before and after heating. By way of comparison, using the material shown in Table 7 and beryllium copper, test pieces were prepared under the same condition aforementioned, and the characteristics were measured in the same method. The results are shown in Table 10. [0083]

Evaluation of high strength titanium copper alloys of the invention

	Evaluation	Superior	Superior	Superior	onbotto	Superior	Superior	Superior	Superior	Superior	Superior	Superior	Poor		Poor	Poor	Poor	Poor	Shrinkage inferior
Thermal expansion/	shrinkage %	90'0	0.05	50.0	600	90:0	90:0	90:0	0.05	0.05	90:0	0.05	0.04	500	0.05	0.04	0.05	0.05	0.11
	Hardness Hv	350	360	370	2/6	360	350	350	360	37	350	350	050	2	340	320	320	310	380
g process	Electrical Conductivity %IACS	10	=		"	12	10	11	12	10	12	12	,,	97	∞	10	9	13	25
Characteristic after aging process	Elongation %	3	,	7	2	0	4	2	3	2	4	3	1	7	-	-	-	2	3
Charact	0.2% proof stress MPa	1180	070.	D#71	1220	1220	1200	1200	1210	1250	1200	1220		720	1220	1100	1100	940	1200
	Tensile strength	1230	000	1290	1300	1290	1260	1270	1200	1310	1260	1280		780	1280	1180	1210	1040	1300
ing process	Electrical Conductivity	1		7	5	s	9	,	,	4	2	4		7	3	s	3	5	16
Characteristic before aging process	Elongation %	,	7	2	-	-	c	,	-	- (	-	,		3	1	-	7	2	SI
Characte	Tensile strength	Mrs	NI I	1170	1180	1160	9711	9	OCT :	0911	1140	0911	2011	650	1140	1060	1170	086	999
	Composition wt%		7311	2.9Ti	3.4Ti	2.9Ti-1.0Zn-	2070	2.511-0.10Cr	3.211-0.20Fe	3.2TI-0.25In	3.1Ti-0.15Sn-	2.9Ti-0.8Zn-	0.25Ni-0.05Sn	1.5Ti	2.8Ti-4.2Zn- 1.30Ni-0.40Sn	2.7Ti-1.0Za- 0.30In-0.15P	3.1Ti-1.5Zn- 0.35Fe-	3.1Ti-1.8Zn-	0.50Sn 1.9Bc-0.25Co-
$\vdash$	ģ	†	_	2	3	4	1	,	0	7	0 6	9	 3	=	12	13	7	2	92

[0084] As can be seen from Table 10, in Nos. 1 to 10 in example 4, the strength after the aging process was equivalent to that of beryllium copper (No. 16), and a high electrical conductivity was obtained. In contrast, with No. 11, the titanium content was less than 2.0% by mass, and the tensile strength was low. In No. 16, the thermal expansion and shrinkage rates were extremely large.

[0085] According to the invention, as described herein, the titanium copper alloy is increased in strength without sacrificing the bending properties, and the required characteristics as the terminal connector for electronic component can be improved, so that a material for a terminal connector of high reliability can be presented. In the examples of the invention, the titanium copper alloy has a tensile strength of 1200 MPa or more and an electrical conductivity of 10% IACS, and it is increased in strength to a level equal to that of beryllium copper, and it is improved so as to be a copper alloy suited for use in terminal connectors for electronic component, in particular, for fork-shaped connector for FPCs, and it is shown to be usable sufficiently as a substitute copper alloy for beryllium copper alloy. IN addition, if the contact of the terminal connector is plated before or after working, the strength is hardly changed, and the effects of the invention are unchanged.